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# CONCERNING A NEW CLASSIFICATION OF TRICYANIDES

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Heidelberg

Translation of "Ueber eine neue Reihe von Tricyaniden," In: Berichte der Deutschen chemischen Gesellschaft, Vol. 22, 1889, pp 803-811



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16. Abstract

A new classification series of tricyanides is presented. Several tricyanides are synthesized by a simple method from aluminum chloride, benzonitrile, and a respective alkyl or phenyl chloride, purified by recrystallization and distillation, and then analyzed. Structural formulae are suggested, and molecular weights, melting points, and boiling points are determined for each.

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# CONCERNING A NEW CLASSIFICATION OF TRICYANIDES

F. Krafft and A. von Hansen

The discovery of certain compounds which surprisingly demonstrate /803* the remarkable phenomenon of "cleavage light" and which have been described by one of us recently in greater detail[1] has motivated a number of further investigations. After pentadecyl paratolyl ketone, $C_{15}H_{31}.CO.C_6H_4.CH_3$, was prepared by the effect of palmityl chloride on toluene in the presence of aluminum chloride, the next goal was to obtain a similar compound using the same method with palmityl chloride and benzonitrile.

Dr. F. Schniewind, who had participated in the experiments mentioned above, was successful in obtaining a product which crystallized excellently, melted at 64°, and boiled at 328° (uncorrected) at a constant pressure of 13 mm, thus appearing likely to have been the desired $C_{15}H_{31}.CO.C_6H_4.CN$: the analysis itself showed very quickly that the compound contained no oxygen but demonstrated on the other hand a comparatively considerable nitrogen content. Since the new substance was nearly as indifferent to saponification with alkali as a carbohydrate would be, the corresponding experiment was conducted with acetyl chloride, benzonitrile, and aluminum chloride in order to clarify the situation. In this case as well, an oxygen-free and nitrogen-rich compound of unusual stability was obtained, which invited further investigation because of the simplicity of its preparation and its definitive characteristics. Since Dr. F. Schniewand had to neglect this subject because of his transfer into technology, we have continued the experiments ourselves and are reporting our preliminary results on this peculiar synthesis. These results indicate that the new classification of compounds is that of the normal tricyanides, previously sought in vain.

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1 F. Krafft, these Berichte XXI, 2266.

* Numbers in the margin indicate pagination in the foreign text.

Methyl Diphenyl Tricyanide, $C_{16}H_{13}N_3$

Two parts aluminum chloride were added to a mixture of 5 parts benzonitrile and 2 parts acetyl chloride which had been cooled to 0° and the entire mixture was then gradually heated to 40-50° over a period of 6 hours and then to about 70° over a half-day in a water bath, at which point all aluminum chloride was dissolved and a moderate development of hydrochloric acid occurred. The resulting yellowish viscous liquid was poured into ice water, and a wax-yellow paste with a /804
peculiar odor, irritating to the point of tears, was precipitated. The mixture was allowed to stand briefly, the water decanted, and the remainder suspended in ether, filtered, and finally distilled after allowing the ether to evaporate. Benzonitrile is the first to come off, then benzoic acid-- for convenience it is best to work under greatly lowered pressure-- and finally at 15 mm pressure a nearly crystalline congealed white mass, generally between 220-230°, corresponding to a boiling temperature of approximately 370° at normal pressure. This last substance is easily purified by recrystallization in ligroin; recrystallization in alcohol is even easier, yielding the compound in splendid slender needles after some standing even though this solution is easily oversaturated; 50 g of the new compound can be obtained from 100 g acetyl chloride, and a larger part of the benzonitrile is recovered.

The preparation melts at 110°, boils at 227° at 15 mm pressure, and when analyzed yields numbers indicating the formula $C_{16}H_{13}N_3$.

| | Values Found | Predicted for $C_{16}H_{13}N_3$ |
|---|---|---|
| C | 77.75 | 77.73 pCt. |
| H | 5.69 | 5.26 » |
| N | 17.25 | 17.01 » |

As can be seen from the following, the substance can be regarded as methyl diphenyl tricyanide: $C_3N_3(CH_3)(C_6H_5)_2$.

The compound possesses basic properties, but only to a slight degree, in spite of the high nitrogen content. The hydrochloride $C_{16}H_{13}N_3.HCl$ can be obtained easily by introducing dry gaseous hydrochloric acid to the benzol solution of the base, whereupon nearly insoluble needles precipitate immediately but break down again when shaken in the cold. These properties can be utilized in determining the hydrochloric acid content. When the hydrochloride is heated to 150°, hydrochloric acid begins to evolve vigorously, and the pure base which is easily identified by its melting point is left behind. --When the alcohol solution of the free base was mixed with a small amount of aqueous hydrochloric acid and then with a platinum chloride solution, the unaltered substance precipitated first, and only after standing the ruby-red crystals of the desired platinum double salt were precipitated. In order to prepare the latter, gaseous hydrochloric acid was introduced into the slightly heated alcohol solution of methyl diphenyl tricyanide and the platinum chloride, which was also in an alcohol solution and slightly heated, was then added: when cooled, the platinum double salt was usually precipiated from the alcohol in small red-yellow crystals. These crystals were filtered, washed with a small /805
amount of cold alcohol, and dried in a vacuum.

| | Values Found | Predicted for $PtCl_4(C_{16}H_{13}N_3.HCl)_2$ |
|---|---|---|
| Pt | 21.50 | 21.52 pCt. |

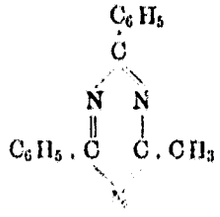
Thus the calculated molecular weight of the compound is 247 ($H_2 = 2$) and that of $C_{16}H_{13}N_3$ is also 247. When the platinum double salt is shaken with a large amount of water, it breaks down even at room temperature and nearly colorless flakes take the place of the red-yellow crystals. These flakes, when filtered and dried, again demonstrate the melting point 110° of the original substance with only trace quantities of the platinum salt. Since one experiment had shown that the methyl diphenyl tricyanide boils practically without decomposition at normal pressures with only a small amount of benzonitrile detectable after several hours of boiling over a direct flame-- and that perhaps only a result of partial overheating-- we conducted a

determination of vapor density at 444° as well. This determination yielded a molecular weight of 244.

The compound demonstrates great stability with respect to potassium hydroxide: only traces of ammonia are released even after prolonged heating, only a little of the compound itself disappears, and the filtrate, after acidification with hydrochloric acid, contains no detectable amount of benzoic acid. A simple experiment thus supplied satisfactory information concerning the nature of the compound. If the compound is refluxed with moderately dilute sulfuric acid (1 : 3 water), the floating oil gradually begins to dissolve. After a few hours a completely clear solution was obtained. Benzoic acid crystallized out upon cooling and was easily identified by its properties as well as its melting (121.5°) and boiling (249.2°) points. The dilute solution is distilled and the distillate contains large quantities of acetic acid along with trace amounts of benzoic acid, as demonstrated by the metal content of precipitated and recrystallized silver salt in a suitable purification method. The distillation remainder was again diluted, admixed with potassium hydroxide, and heated; ammonia was evolved. The added hydrochloric acid then combined with the compound and the platinum double salt which resulted after addition of the platinum chloride solution and subsequent concentration in the water bath demonstrated the composition of pure ammonium chloroplatinate. (43.82% Pt found instead of 43.89%.)

The saponification of the substance as performed under suitable conditions thus yielded simply benzoic acid, acetic acid, and ammonia. Since the compound is oxygen-free, it can be assumed in light of numerous analogies that the acetic acid originates from a constituent $CH_3.C$ residue, the benzoic acid from a $C_6H_5.C$ residue-- or, more correctly, /806 from two of each of these residues, according to the results of the analysis and molecular weight determination. The dissociation thus completely agrees with the empirically determined molecular formula $C_{16}H_{13}N_3$. One obtains: $2(C_6H_5.C)^{III} + (CH_3C)^{III}$ and in addition, by simple substraction from the formula, 3 nitrogen atoms $(N_3)^{IX}$. Since the otherwise remarkably stable compound dissociates so easily in

dilute sulfuric acid, the most likely preliminary formulation, in close dependedence on the customary criteria, would have this appearance:



This formula satisfactorily illustrates the origin of the compound from the given starting materials: the source of the third nitrogen atom is admittedly somewhat uncertain, but the presence of large quantities of benzoic acid during purification (see above) already indicates a way of solving this problem.

Ethyl Diphenyl Tricyanide, $C_{17}H_{15}N_3$

Even before the nature of the previously described compound was sufficiently clarified, corresponding experiments were conducted with propionyl chloride and certain other acid chlorides, partly in order to accelerate the discoveries and indications and partly to determine whether this was a general sythetic reaction. To a cooled mixture of 5 parts benzonitrile and 2.5 parts propionyl chloride, 2.5 parts aluminum chloride were gradually added and the mixture was slowly heated to 70° in exactly the same manner as in the previous case. The processing and purification of the propionyl chloride derivative was performed exactly the same as for the acetyl compound. Thus we obtained a well-crystallizing compound with a melting temperature of 67°, a boiling temperature at 15 mm pressure of 233-234°, and a composition $C_{17}H_{15}N_3$: ethyl diphenyl tricyanide by analogy.

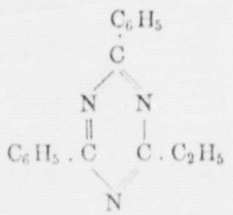
| | Values Found | Predicted for $C_{17}H_{15}N_3$ |
|---|---|---|
| C | 78.11 | 78.16 pCt. |
| H | 6.02 | 5.75 » |
| N | 15.70 | 16.09 » |

The hydrochloride salt can be formed in this case also by introducing hydrochloric acid in the benzol solution of the base. The salt precipitates here also, although not as completely as with the homolog /807 below, in crystalline form. It demonstrates the same stability as the salt described above. The likewise easily dissociated platinum double salt was prepared with the same precautionary measures as the methyl diphenyl tricyanide salt, since it was nearly completely dissociated also by shaking with cold water in the tricyanide, hydrochloric acid, and platinum chloride solution. The metal determination supported the above molecular formula:

| | Values Found | Predicted for $(C_{17}H_{15}N_3HCl)_2PtCl_4$ |
|---|---|---|
| Pt | 21.18 | 20.88 pCt. |

The vapor density could be determined directly by the air-displacement method for this substance also. For the molecular weight, we found: 258 ($H_2$ = 2) instead of 261 (as reported for $C_{17}H_{15}N_3$); Rapid operation is necessary for this determination, since the substance begins to dissociate quickly in air at normal pressure and at the boiling temperature of sulfur.

The compound appears to be the ethyl diphenyl derivative of the as yet hypothetical hydrogen tricyanide $C_3N_3H_3$:




Propyl Diphenyl Tricyanide, $C_{18}H_{17}N_3$

The next member of this homologous series was prepared from 5 parts benzonitrile, 3 parts normal-butyryl chloride, and 2.5 parts aluminum chloride. The mixture was heated very gradually from 0°

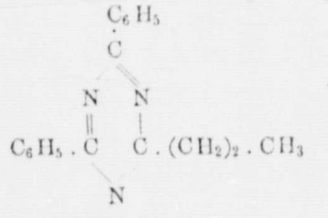
to 60°, the hydrochloric acid development lasting as in all other cases approximately half a day, and finally it was heated for some additional time to 70-80°. The substance plus additional purification crystallized excellently out of alcohol, melted at 78.5°, and boiled at 239° at a pressure of 15 mm. The analysis yielded values which agree with the formula $C_{18}H_{17}N_3$.

| | Values Found | Reported for $C_{18}H_{17}N_3$ |
|---|---|---|
| C | 78.61 | 78.55 pCt. |
| H | 6.41 | 6.18 » |
| N | 15.12 | 15.27 » |

Since the platinum double salt was dissociated by water in this case, too, it was precipitated in alcohol as in the previous cases, and no difficulty was experienced in the pure production of the substance, which precipitated in small red-yellow needles. /808

| | Values Found | Reported for $(C_{18}H_{17}N_3.HCl)_2PtCl_4$ |
|---|---|---|
| Pt | 20.29 | 20.27 pCt. |

The vapor density could be determined directly in this case also from the air displacement at the boiling temperature of sulfur, as it was determined in the first preparations, and we found: 280 ($H_2$ = 2) compared to the calculated value of 275 for $C_{18}H_{17}N_3$. The compound dissociates rapidly when heated with moderately diluted sulfuric acid. The unmistakeable odor of butyric acid is noticeable after only a few minutes; everything dissolves after some time, benzoic acid crystallizes out upon cooling, and ammonia is evolved with the addition of alkali to the filtrate. The most plausible formulation of this compound would hence be:



Hexyl Diphenyl Tricyanide, $C_{21}H_{23}N_3$

Heptyl chloride (4 parts) reacts with benzonitrile (5 parts) and aluminum chloride exactly as in the preceding cases; no difficulty is encountered here in the purification. All members of this series demonstrate slight superfusion phenomena; when freshly prepared, the hexyl diphenyl tricyanide remains liquid for a long time at room temperature following melting or distillation. Only after the introduction of a seed crystal or during extreme cooling does it coalesce to a solid crystal mass.

The substance melts at 44°, which is considerably lower than its other homologs. The peculiar sinking of the melting point in consecutive series members which is familiar in the fatty acid series is repeated here in this order; from this point on in this series, as well as in the fatty acid series, the melting point begins to climb again slowly, as demonstrated by the palmitic acid derivative (see below), which melts at 64°. The boiling point of hexyl diphenyl tricyanide is 265° at 15 mm pressure. It demonstrates the expected composition of $C_{21}H_{23}N_3$.

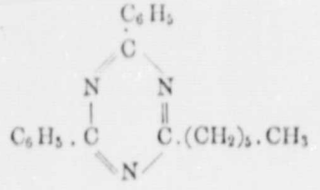
| | Values Found | Reported for $C_{21}H_{23}N_3$ |
|---|---|---|
| C | 79.51 | 79.49 pCt. |
| H | 7.51 | 7.26 » |
| N | 13.13 | 13.25 » |

The metal determination of the platinum double salt yielded: /809

| | Values Found | Reported for $(C_{21}H_{23}N_3HCl)_2PtCl_4$ |
|---|---|---|
| Pt | 18.45 | 18.63 pCt. |

The rational formula of hexyl diphenyl tricyanide would be

written, as in the above cases, as:



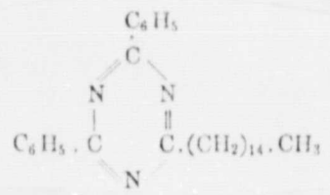
Pentadecyl Diphenyl Tricyanide, $C_{30}H_{41}N_3$

As mentioned above, these compounds were developed in an attempt to achieve the synthesis of a ketone, $C_{15}H_{31}.CO.C_6H_4.CN$. Three parts aluminum chloride were added to a mixture of 5 parts benzonitrile and 3 parts palmityl chloride and the entire solution was heated for 60 hours, beginning at approximately 40° and increasingly warmer, ending with a period of time at 100° for as long as noticeable hydrochloric acid evolution continued. When the cooled mass, which was very viscous, was poured into slightly acidified water, dark flakes precipitated. This precipitate was suspended in ether and subjected to distillation as in the previous preparations. The unreacted benzonitrile and all else which vaporized below 300° at 15 mm pressure was collected separately and the remainder recrystallized from boiling alcohol. About 30 g of a slightly colored, nearly pure product was obtained from 60 g palmityl chloride. This product boiled at 327-328° at 15 mm after two rectifications. The compound dissolves readily in both ether and hot alcohol, and with difficulty in cold alcohol. A recrystallization from isobutyl alcohol proved to be suitable for the removal of contaminants which would otherwise become noticeable as persistent turbidity during the melting point determination. The resulting crystals formed in the cold were flaky bulbous hollows which, after filtering, alcohol washing, and drying, melted at a constant 64°.

The figures obtained from the analysis agree so well with the formula $C_{30}H_{41}N_3$ that there can be no doubt concerning the composition of this compound.

| | Values Found | Reported for $C_{30}H_{41}N_3$ |
|---|---|---|
| C | 81.01 | 81.26 pCt. |
| H | 9.30 | 9.25 » |
| N | 9.11 | 9.48 » |

Saponification could be observed neither during heating with /810
alcoholic potassium hydroxide for 6 hours at 120-125° nor during melting with potassium hydroxide. Pentadecyl diphenyl tricyanide also demonstrated far more stability in moderately diluted sulfuric acid than its lower homologs. A platinum double salt could not be produced. -- Nevertheless it is possible to draw conclusions concerning its rational formula by analogy to the previous investigations and regard it as a pentadecyl diphenyl tricyanide.




It might be noted here that cyaphenene (melting point 231°)(prefrom benzonitrile and concentrated sulfuric acid) boils at approximately 285° at 15 mm.

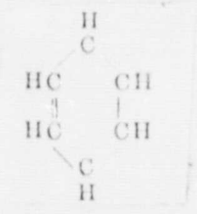
When it is heated with sulfuric acid, the compound cyaphenene does give off benzoic acid and ammonia, although not readily. A satisfactory explanation for failure to produce a platinum double salt from cyaphenene despite all efforts can be found if cyaphenene is regarded as a tricyanide in which a negative phenyl group is substituted for the positive alkyl radicals of the already very weak bases considered above. We would like to reserve definitive statements

concerning this viewpoint for later. The fact that basic properties depart from cyaphene is already well-known.

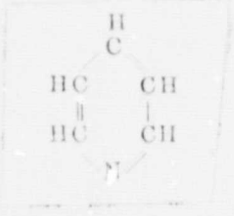
If one considers the described compounds, which could easily be added to in many ways, as derivatives of the preliminarily hypothetical "hydrogen cyanide", $C_3H_3N_3$, then one immediately becomes aware of an inconsistency in the classification of carbon compounds, the elimination of which should motivate no small number of investigations. It is the nomenclature for cyanides and tricyanides added to this [illegible] date from which no one has previously deviated for known reasons of expediency. Hydrogen cyanide is related to hydrogen tricyanide in the same way that acetylene is related to benzene. At least one has the formulae:

$$CH{:}CH \text{ and } C_6H_6; \quad CH{:}N \text{ and } C_3H_3N_3.$$

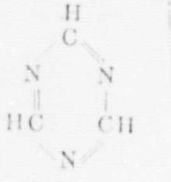
No systematician would consider it proper to place the "aromatic compounds" right next to acetylene and its derivatives: yet an even greater difference exists in actuality for the cyanides and tricyanides as well; the only difference is that here the transitions have been known longer and by many. -- The further pursuit of this subject does not belong here; therefore we simply submit a collection of the formulae:



benzene



pyridine



"hydrogen tricyanide"

The research field "hydrogen tricyanides", from which to date none of the fellow colleagues have concerned themselves with the above sharply defined viewpoints, has already been attacked in the indicated sense from many directions.